Research Article

INDONESIAN CHIMICA LETTERS

DOI: 10.19184/ICL.v1i1.6

Effect of pH in Coagulation Bath on Polysulfone-based Membrane Formation and Its Performance Characteristics

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Abstract: One of the factors that determine the formation of the membrane is the solution in the coagulation bath (non-solvent). In this study, the effect of pH treatment on the coagulation bath solution on membrane formation and its effect on membrane performance will be studied. The pH of the coagulation bath used was pH 1, 6.8 and 12. As the results, physically the three pH treatments produced the same white (opaque) membrane. Through morphological analysis, it appears that the three pH treatments produced an asymmetric membrane consisting of a top layer and a sub layer. The surface of the membrane with pH 1 treatment showed a denser surface than the pH 6.8 and pH 12 treatments. The results of the membrane performance characterization showed that the membrane permeability coefficient of the membrane with pH treatment was in the following order pH 1 < pH 12 < pH 6.8. While the value of the rejection coefficient showed that the membrane treated at pH 1 did not detect rejection because there was no permeate coming out, while at the treatment at pH 6.8 and 12, the rejection coefficient values were 74% and 76%, respectively.

Keywords : coagulation bath, pH, asymmetric membrane, permeability coeficient, coefficient of rejection.

INTRODUCTION

Membrane technology is one of the rapid develop separation technologies. Compared to conventional separation technologies such as distillation and extraction, membrane technology has advantages such as low energy consumption, can be carried out continuously, and easy to scale up [1].

One of the important factors in membrane technology is the membrane preparation. The preparation of membranes can be viewed from the starting materials and the method. Based on the starting materials, membrane materials can be derived from organic and inorganic materials [1]. The organic and anorganic materials can be further grouped into synthetic and non-synthetic (nature-based) materials. One type of material that is widely used in the membrane preparation is polysulfone, due to have mechanical and thermal stability and is easily casting into membranes for various applications [1, 2].

The formation of the membrane is influenced by factors such as polymer concentration, type of solvent and its composition, temperature, additives, and composition in the bath coagulation. The factor of the solution composition in the coagulation bath on the morphology and performance of the membrane has been investigated. In addition to the composition of the solution, setting the pH of the solution also affects the formation of the membrane in terms of surface properties, porosity and permeability. Zhao et.al, have studied the effect of the pH of the coagulation bath on the formation of PSF/PANI composite membranes, water flux and rejection of protein (BSA) [3]. The results showed that increasing the pH increased porosity, but decreased protein rejection slightly. Similar results were also shown by the PVDF/fluorocarbon membrane blend with surfactant FS-50. This study examines the effect of pH on the formation of PSF membranes and characterizes its performance from the value of its permeability and membrane rejection of 70-80 kD Dextran solution [4].

METHODS

Materials

Udel Polysulfone (PSF) (Mw = 35000 Da) was obtained from Union Carbide. N.N-dimethylacetamide (DMAc), Hidrochlorid acid, sulfuric acid, sodium hydroxide, phenol were purchased from Merck. Dextran (Mw = 100-200 kDa) was purchased from sigma Aldrich, Polyethylene glycol (Mw = 400 Da) (PEG 400) was purchased from Brataco chemicals and distilled water.

Membrane Preparation

The membrane preparation was carried out using the inversion phase teqnique followed the procedure of Bambang Piluharto et.al with slight modifications [5]. The preparation of the membrane was started with prepare a dope solution consist of PSF, DMAc and PEG 400 with a composition of 18%, 64% and 18%. Next, the dope solution was cast on glass plate followed by immersion in a coagulation bath. In this case, the pH of the coagulation bath was adjusted to obtain pH 1, pH 6.8 and pH 12. Then, the membranes were dried at room temperature.

Morphology Analysis

Morphological analysis was carried out to observe the surface structure and cross-section of the membrane. Observation was carried out by Scanning electron microscope (SEM) at Pusat penelitian dan pengembangan Geologi kelautan, Bandung.

Characterization of Membrane Performance

Determination of Membrane Permeability

Membrane permeability was determined by measuring the water flux at various pressures (1, 2 and 3 atm). Coefficient of Permeability is calculated from the slope of linier curve according to the following equation:

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$$J\_v = Lp \times \Delta P \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ (1)$$

Where Jv is water flux (L/m2.h); ΔP is pressure gradient dan Lp is Coefficient of Permeability [6].

Determination of water flux

Water flux is the amount of permeate produced per unit surface area per hour which is formulated as follows:

$$J\_v = V/(A \times t) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Where Jv is water flux (L/m^2.jam), V is permeate volume (L), A is surface area of membrane (m^2) dan t is the time required to reach a certain volume of permeate (h).

Determination of membrane rejection (%)

Membrane rejection (%) was carried out using Dextran (Mw = 100-200 kDa) as feed solution. The amount of dextran in retentate and permeate was determined using spectrophotometric methods. Determination of membrane rejection (%) is formulated as follows:

$$R = (1 - C_{permeate}/C_{retentat}) \times 100\% \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ (3)$$

Where R is membrane rejection, $C_{permeate}$ adalah konsentrasi dekstran dalam permeate dan $C_{retentate}$ adalah konsentrasi dekstran dalam retentate.

RESULTS AND DISCUSSION

Physically the casting membranes include color and thickness were showed on Table 1. All of membranes have the same color, but there aere slight difference in thickness. In here, pH of 1 (acid) have thicker than both of pH of 6.8 (neutral) and 12 (base). demixing process at pH 1 is estimated take place as delay demixing lead to thick membrane formation [5].

Table 1. Physical properties of membranes in various pH coagulation bath

pH of coagulation bath	colour	Thickness (mm)
1	opaque	0,0074
6.8	opaque	0.0060
12	opaque	0.0065

Morphology analysis

This analysis was carried out by observing the membrane surface (top and bottom) and its cross section. Figure 1 is the result of SEM images for membranes with various pH in a coagulation bath.

pH of coagulation bath	Top surface	Bottom surface	Cross section
1			
6.8			
12			

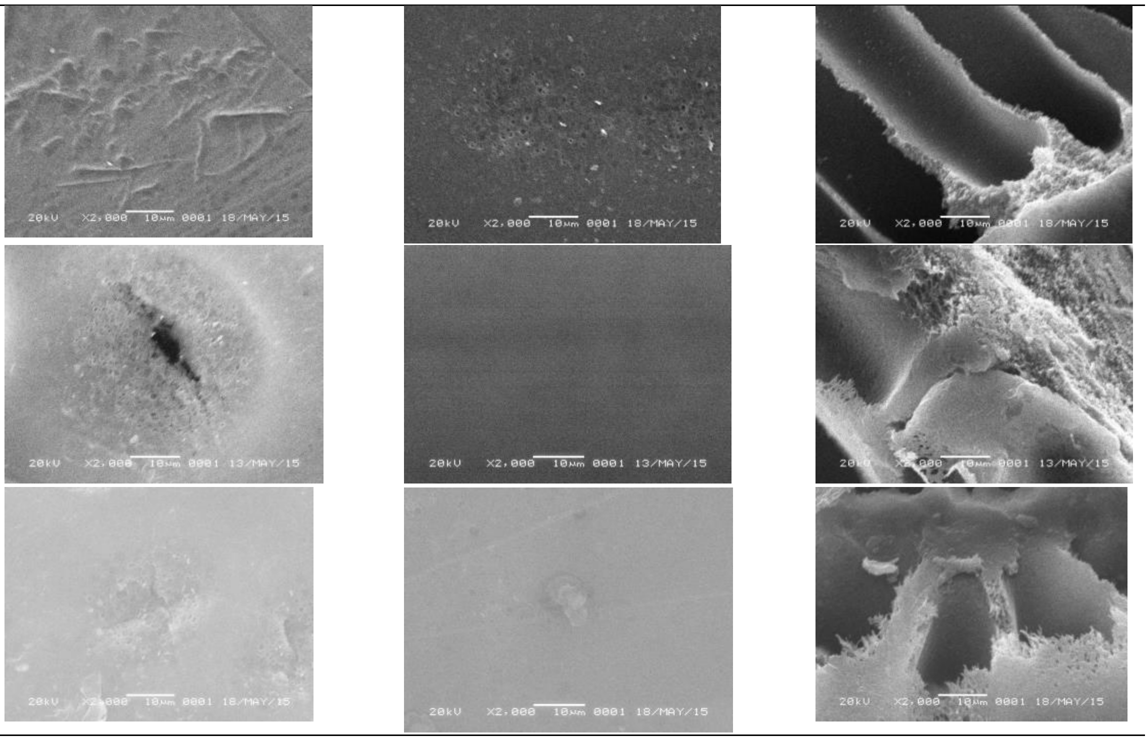

Figure 1. Top, bottom surface and cross section of SEM image of membranes

Figure 1 shows that the membrane at pH of 1 have the top layer with dense structure and do not show the presence of pores formed, whereas in cross section finger like is formed. The membrane at pH of 6.8 has the top layer with pores evenly in the surface. In the cross section, macrovoids are formed that influence on the separation process. The membrane at pH of 12 show that pores formed evenly but the pore size was small at the top layer, in the cross section larger macrovoids were formed than at pH of 6.8.

Characteristics of Membrane Performance

Permeability Coeficient

Using equation (1) the coefficient of membrane permeability on various pH in the coagulation bath is obtained as Table 2.

Table 2. The coefficient of membrane permeability on various pH in the coagulation bath

Membran ID	pH of coagulation bath	Coefficient of permeability (L m^{-2} jam^{-1} atm^{-1})	Coefficient of Regression (R^2)
Membran I	1	0.0099	0.98
Membran II	6.8	0.0516	0.99
Membran III	12	0.0342	0.94

Based on Table 2, various pH in the coagulation bath give different results on the value of the permeability coefficient. The coagulation bath with pH of 1 gives the smallest permeability coefficient value compared to pH 6.8 and pH 12. The permeability coefficient value is influenced by the shape of the membrane structure. The membrane structure can be observed from the parameters of the thickness and porosity of the membrane [6]. This result is in line with the results of the membrane thickness shown in Table 1 where pH 1 has the highest thickness.

Determination of membrane rejection on Dextran solution (Mw 100-200 kDa)

Measurement of membrane rejection using a dextran solution (Mw = 100-200 kDa) with a concentration of 1000 ppm. The results obtained are shown in Figure 2.

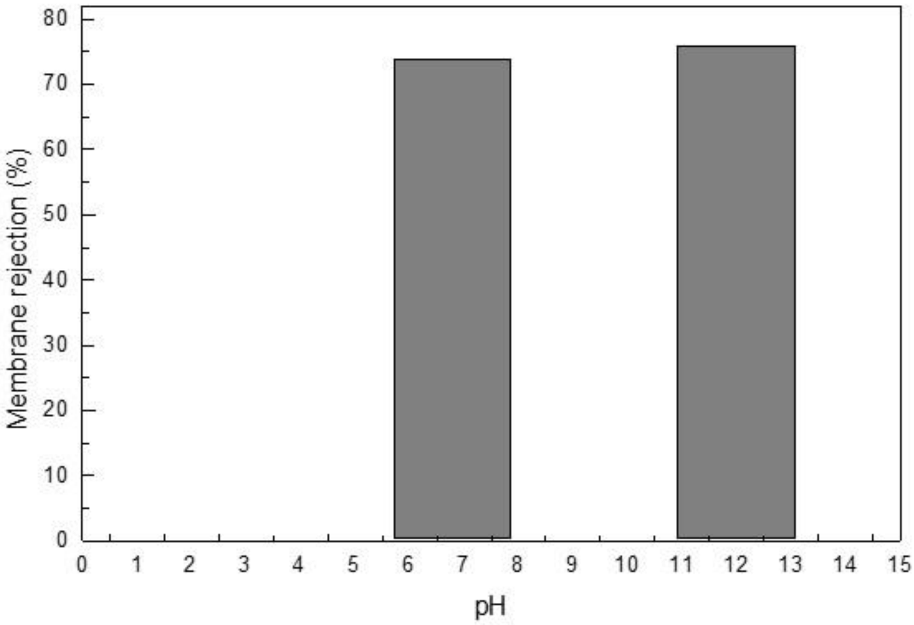

Figure 2. Membrane rejection of membranes in various pH in coagulation bath

Based on Figure 2, it can be seen that the membrane rejection of the membrane I (pH of 1) not available result, due to absence of permeate. This indicates that the membrane obtained by treating pH of 1 produces a dense membrane. Meanwhile, membrane rejection at pH 6.8 resulted in 74% rejection of dextran solution and pH 12 with 76% rejection. These results are in line with the characterization of the physical properties and the coefficient of permeability (Table 1 and 2).

CONCLUSION

Based on the results obtained, the following conclusions:

1. Various pH in the coagulation bath produces a membrane with an asymmetric structure.
2. Coagulation Bath under pH of 1, produced membrane with lowest coefficient permeability followed by pH of 12 and pH of 6.8.
3. Membrane rejection for membranes with Coagulation Bath under pH of 1 was estimated a dense membrane, whereas on pH of 6.8 and pH of 12 produced the membrane rejection are 74% and 76 % respectively.

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